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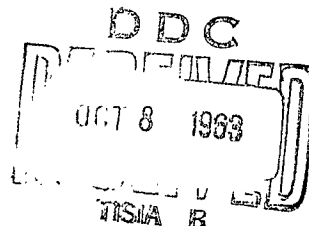
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Abstract for International Conference on Current Problems in Crystal Physics, Massachusetts Institute of Technology, July 1-6, 1957.

(6) Some New X-Ray and Neutron Studies of

Hydrogen Bonding\*

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Three-dimensional refinement on the IBM 704 machine of x-ray analyses of cycloserine hydrochloride (an antibiotic), zinc aspartate trihydrate, and urea phosphate has revealed interesting H-bond systems in these crystals. The cycloserine-HCl analysis<sup>1</sup> reveals six short intermolecular distances, indicating O-H...O, N-H...O and N-H...Cl bonds; but only four hydrogens are available for formation of these bonds. F<sub>O</sub>-F<sub>C</sub> syntheses indicate the existence of two "bifurcated" H-bonds — i.e., hydrogens shared by three atoms. Crystal-chemically, this situation can be described in terms of a three-coordination about hydrogen rather than two. The same situation is found, twice, in urea phosphate, described below.

A three-dimensional refinement of the structure of zinc aspartate trihydrate, in which the phase problem was solved by means of the P<sub>s</sub>(u) function for anomalous scattering<sup>2</sup>, shows hydrogen positions, and reveals H-bonding which leads to an interesting ring structure and recalls the proposal of Steward and Thompson<sup>3</sup> for a cyclic structure for asparagine.

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The structure of urea phosphate shows very strong H-bonding throughout. The interatomic distances were calculated by means of a new IBM 704 program<sup>4</sup>. Seven hydrogens are available for nine short bonds — again indicating hydrogen sharing by two bonds, in two cases.

The structure of ferroelectric Rochelle Salt has been solved, by a joint x-ray<sup>5</sup> and neutron analysis<sup>6</sup>. The neutron study employed the technique of isomorphous hydrogen-deuterium replacement<sup>7</sup>; and X-RAC maps have been computed using  $F^{(H)} - F^{(D)}$  and  $F^{(H)} + F^{(D)}$  data, where  $F^{(H)}$  refers to structure factors for a hydrogen-containing crystal and  $F^{(D)}$  refers to analogous factors for the crystal in which ten of the twelve hydrogens have been replaced by deuteriums<sup>6,7</sup>. These maps independently confirm the correctness of hydrogen-deuterium positions and the coordinates of all other atoms. The contribution of the hydrogen (or deuterium) on the second central hydroxyl group of the tartrate ion to the spontaneous polarization is confirmed<sup>8</sup>.

Hydrogen positions have been found in the tetragonal phase of ammonium dihydrogen phosphate, by neutron diffraction<sup>9</sup>. The interesting feature of the O-H...O bonds here is that the hydrogens do not lie on a line connecting the two O's.

Very short intermolecular distances appear in the structure of the explosive HMX, cyclotetramethylene tetranitramine<sup>10</sup>; distances of 3.03 Å and 3.15 Å are found between one O of a nitro group and methylene C's of two adjacent molecules. This structure has recently been further refined by the IBM 704 least-squares program, and the short distances are confirmed. It is demonstrable that H's are not involved in these remarkably short bonds. This compound must be a self-intermolecular complex;

and, if so, this is the only reliable example of short intermolecular distances in such a complex<sup>11</sup>. The structures of these organic intermolecular complexes, and the physical nature of the bonding — in which, in general, hydrogens are not involved — is a foremost problem in modern valence theory; and further x-ray studies of these compounds is a pressing matter.

Some problems in the stereochemistry of hydrogen bonds are described, as are problems of dielectric anomalies and other transition phenomena involving H-bonds. The mechanisms of the ferroelectric transitions in the ammonium and organic amine alums,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Cd}_2(\text{HN}_4)_2(\text{SO}_4)_3$ ,  $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$  and isomorphs, and thiourea, the nature of the polarization in guanidinium aluminum sulfate hexahydrate and isomorphs, and the anomalies in the hydrogen halides, are of particular interest.

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<sup>3</sup>F. C. Steward and J. F. Thompson, Nature 169, 739 (1952).

<sup>4</sup>V. Vand and R. Pepinsky, to be published.

<sup>5</sup>F. Mazzi, F. Jona and R. Pepinsky, in press, Zt. f. Krist.

<sup>6</sup>B. C. Frazer, H. R. Danner and R. Pepinsky, to be published.

<sup>7</sup>R. Pepinsky, Hydrogen-Deuterium Replacement in Neutron Diffraction Analysis. Eleventh Annual Pittsburgh Diffraction Conference, November, 1953.

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<sup>9</sup>L. Tenzer, B. C. Frazer and R. Pepinsky, Am. Cryst. Assoc., French Lick Meeting, June, 1956.

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